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A New Upper Limit to the Thermoelectric Figure-of-Merit

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10.1 Introduction

Thermodynamics does not place any upper limit on the dimensionless thermoelectric figure-of-merit, *ZT*, but for many years it was impossible to find values significantly greater than unity. Empirically, one can predict an upper bound by combining the best electronic properties of any known crystalline material with a phonon conductivity that is typical of glass. By this means, one arrives at a highest value of *ZT* equal to about four. Recently, however, it has been demonstrated that certain low-dimensional structures can have values of the figure-of-merit that exceed those found in bulk materials. This allows us to upgrade our predicted limit for *ZT* to, perhaps, 20. If this value were eventually achieved, thermoelectric energy converters would have no less than about 50% of the efficiency of a Carnot cycle. The performance would then be comparable with the best that is likely to be achieved using converters that are based on the vacuum diode.

Several attempts have been made in the past to estimate the maximum thermoelectric figure-of-merit that will ever be reached. There is no restriction placed on the value of *ZT* by thermodynamics since, if this quantity ever became infinite, the thermoelectric efficiency would still be no greater than that of the Carnot cycle. Realistic considerations suggest that thermocouples will never approach this ideal efficiency. At room temperature, the best thermoelectric materials are solid solutions based on bismuth telluride.[1] A value of *ZT* equal to about one was established for these materials in the late 1950s and has not been improved upon since then. Although marginally larger values have been found for other compounds and alloys at higher temperatures, it is true to state that, at the present time, the greatest dimensionless figure-of-merit for bulk materials is of the order of unity under ordinary conditions. There are, however, some indications that larger values of *ZT* might be reached in the future. For example,

a value in excess of two has been observed at high pressures for p-type $Sb_{1.5}Bi_{0.5}Te_3$.[2] Using a conservative estimate for the effect of pressure on the lattice conductivity (this quantity not being measured) it was deduced that the dimensionless figure-of-merit at 9 GPa is equal to 2.2. It is not suggested that it is practical to operate thermoelectric devices at high pressures but this work shows clearly that much larger values of ZT than unity are possible.

The efforts to predict the greatest figure-of-merit that will ever be reached are based on the supposition that the lattice conductivity, λ_L, might have the lowest value that is ever found in the condensed state. Slack[3] has set a lower bound for the mean-free path of the phonons of the order of the lattice spacing. Combining this with typical values for the specific heat and the speed of sound, the minimum lattice conductivity should be no more than about 0.1 to 0.2 W/m K. This lattice conductivity is then combined with a maximum value for the power factor, $\alpha^2\sigma T$. Here, α is the Seebeck coefficient and σ is the electrical conductivity. The power factor depends on the quantity $\mu(m^*/m)^{3/2}$, where μ is the carrier mobility and m^*/m is the ratio of the effective mass to the free electron mass. The highest observed value for $\mu(m^*/m)^{3/2}$ is that for electrons in Bi and is equal to 0.075 m^2/V/sec. One may also suppose that the energy gap is large enough for the Seebeck coefficient to be optimized without having to take into account the minority carriers. These assumptions lead to a dimensionless figure-of-merit equal to four.[1]

When such an upper limit was first proposed, it was thought unlikely that the required combination of properties would ever be found. However, recent advances in the selection of materials and in novel techniques, such as those related to low dimensionality, have increased the probability that a value of ZT equal to four will, in fact, be reached. Perhaps it may even be possible to raise the upper bound for the figure-of-merit in the light of these developments. Our present objective is to investigate this possibility. Our discussion will refer specifically to Peltier cooling at ordinary temperatures but our conclusions should be equally applicable to the generation of electricity using the Seebeck effect.

10.2 New Materials

Most of the thermoelectric research during the past 50 years has been directed towards the discovery of new materials with improved properties. This research has been assisted by the adoption of certain guidelines. The first useful pointer was the high atomic weight rule. Ioffe[4] showed that, within a given set of elements or compounds, the lattice thermal conductivity decreased with increasing mean atomic weight. It was also suggested[5] that the ratio of carrier mobility to lattice conductivity would increase with the atomic weight. These ideas led to the choice of bismuth telluride as a thermoelectric material.[6,7]

The dimensionless figure-of-merit, ZT, is the ratio of the power factor, $\alpha^2\sigma T$, to the total thermal conductivity, λ, which is the sum of the electronic component, λ_e, and the lattice component, λ_L. The electronic component is related to the electrical conductivity in more or less the same way for all electrical conductors but the lattice component is an independent quantity. Bismuth telluride has one of the highest values of the power factor at ordinary temperatures and a low value for the lattice conductivity, particularly when it is alloyed with isomorphous compounds. Nevertheless, its lattice conductivity remains considerably greater than the predicted minimum value.[3,8]

It is found that compounds with empty spaces in their crystal structures can have very low values for the lattice conductivity. The voids may be occupied by loosely bound atoms, which are known as rattlers. Such systems bear the acronym PGEC (phonon glass–electron crystal) implying that these have a lattice conductivity that is characteristic of an amorphous material combined with the typical electronic properties of a crystal. Examples of PGECs are to be found among the skutterudites and clathrates. Some of these materials are semiconductors with Seebeck coefficients of the order of ± 200 μV/K or more and have reasonably large power factors. Since these generally display rather low values of the lattice conductivity, they often have good values of the figure-of-merit, particularly at high temperatures. For example, $ZT = 1.1$ has been observed for a Eu-filled skutterudite at 700 K[9] and similar values have been found for other skutterudites and some of the clathrates.[10] Even though these materials have a thermal conductivity which is lower than that of the bismuth telluride alloys, they are inferior to the latter

at room temperature because of a somewhat smaller power factor. Their importance lies in the fact that they show the validity of the PGEC concept.

10.3 Low-Dimensional Systems

While this work on new compounds has been in progress, there have also been a number of attempts to produce thermoelectric materials in which at least one of the dimensions is not much greater than the lattice constant. This should lead to changes in the electronic band structure that may be favorable and at the same time, there may be a reduction in the lattice conductivity. Some of this work has led to most promising results. For example, Harman et al.[11] have produced an n-type quantum dot structure based on PbSe–PbTe and have observed $ZT = 1.6$. It is significant that a couple made from this material in conjunction with a metallic leg produced a cooling of about 44 K using the easily managed current of 700 mA. The performance is all the more remarkable because, in the bulk form, the PbTe–PbSe alloys are inferior to the bismuth telluride alloys at ordinary temperatures.

Equally interesting is the even larger figure-of-merit for a p-type superlattice based on Bi_2Te_3 and Sb_2Te_3.[12] ZT was found to be equal to 2.4 with current flowing in the cross-plane direction. Most of the improvement is attributed to the reduction in the lattice conductivity to a value of about 1/5th of that in bulk samples. At 0.22 W/m K, this quantity seems to be approaching the minimum value. Because the flow is in the *c* direction, the power factor is actually less than it would be in a bulk crystal with the more favorable current flow in the plane of the *a* axes. The anisotropy of the electrical conductivity is even stronger for n-type material and for this reason the n-type superlattice has a value of ZT equal to no more than 1.6.

Ghoshal et al.[13] have approached the problem of making thermoelectric nanostructures in a different way. They applied multiple point contacts to the flat surfaces of p-type and n-type bismuth telluride alloys. The radius of each contact was typically 0.6 μm, although this quantity could not be maintained at a uniform value. There seemed to be two regimes of operation. In one regime, tunneling between the metal and semiconductor was thought to occur, with little contribution from the phonons to the transfer of heat. In the other regime, the metal was supposed to make intimate contact with the semiconductor, the lattice conductivity being dominated by surface scattering. Whatever the actual mechanism at work, the cooling effect on the passage of an electric current is superior to that observed when the same materials are used in conventional thermocouples. Ghoshal et al. found the value of ZT to be 1.4 compared with 0.84 for commercial modules made from the same materials. ZT was considered to be higher (estimated at 1.7) for the p-type side than for the n-type side, because point contacts necessarily lead to transport in the preferred *a* direction and the less preferable *c* direction. The device seems to have practical potential since a temperature difference of over 60 K was observed for a current of 400 mA. This work is significant in demonstrating that the figure-of-merit can be improved without resort to the usual techniques for producing nanostructures.

As we shall see, it is really the work on low-dimensional thermoelectrics that gives greatest cause to hope that values of ZT in excess of four will eventually be achieved.

10.4 The Maximum ZT for Low-Dimensional Structures

Although there seems to be little doubt that the work on new *bulk* materials will eventually lead to substantial improvements in the figure-of-merit, it does not alter our previous conclusions about the limit on ZT. None of the new materials has a power factor that is much greater than that of bismuth telluride. The promising results are due entirely to the very low lattice conductivities that have been observed. However, our limit of $ZT \approx 4$ is already based on the assumption that the lattice conductivity has its minimum value. The new materials should assist in reaching this limit but not exceeding it.

A new factor arises when low-dimensional structures are considered. There seems to be no reason why the power factor should not be improved as a result of changes in the electronic band structure following confinement.

It is unlikely that any worthwhile low-dimensional thermoelements will make use of materials that do not already have reasonably large figures-of-merit in the bulk state. Moreover, it may not matter if the energy gap, E_g, in a large crystal is too small to allow the optimum Seebeck coefficient to be reached since the gap may well increase as the size is reduced. Thus, it is possible that nanostructures based on Bi or *Bi–Sb* may have exceptionally large figures-of-merit. As has already been pointed out, Bi has the best known value of $\mu(m^*/m)^{3/2}$ for any material. It is only the fact that it is a semimetal with overlapping valence and conduction bands that makes it inferior to bismuth telluride in its bulk form. Certain alloys of Bi–Sb have positive energy gaps that are just large enough for these materials to be used as low-temperature thermoelements, the reduction in the lattice conductivity also being beneficial.

The theoretical work of Lin et al.[14] on Bi nanowires is considered highly significant. These authors calculated the changes to the band structure as the diameter of the wires is reduced. They then determined the Seebeck coefficient as a function of carrier density and applied the results to the determination of ZT at 77 K. The calculations yielded $ZT = 6$ for n-type Bi wires along the trigonal axis when the carrier concentration is $10^{18}\,\mathrm{cm}^{-3}$ and the diameter is 5 nm. Lin[15] has stated that the Seebeck coefficient is about $-400\ \mu$V/K, much greater than the value for crystalline Bi, whether doped or undoped, in any direction. The high power factor arises from an electrical conductivity of about $3.4 \times 10^6\ \Omega^{-1}\,\mathrm{m}^{-1}$ that, in turn, is the result of an enlarged density of states. The lattice conductivity was not supposed to be particularly small. The work has been extended by Rabin et al.[16] to Bi–Sb nanowires.

This work seems to be a good starting point for a reassessment of the highest possible value of ZT. We shall suppose that the electronic properties that have been calculated for Bi nanowires can be achieved in some other low-dimensional system in which the lattice conductivity is at its minimum. Rather than assuming the Slack or Cahill value for the minimum in a multicomponent system, we shall suppose that the interfaces might have an important part to play. The interface thermal conductances have been given by Cahill et al.[17] for a number of pairs of materials. The lowest values, over a wide range of temperatures, are of the order of 30 MW/m^2 K. Now suppose that we are dealing with superlattices that have a period of, say, 5 nm. Then there will be 2×10^8 interfaces per m. If the resistance were solely due to the interfaces, the lattice conductivity could be as low as 0.15 W/m K. This is of the same order as the Cahill minimum so that it is still justified in setting 0.1 W/m K as a lower limit for the phonon conductivity.

Perhaps we should also consider the approach to the determination of the minimum lattice conductivity for superlattices that was made by Simkin and Mahan.[18] According to these authors, the lattice conductivity falls with the superlattice period until the latter becomes equal to the mean-free path of the phonons. As it becomes still smaller, interference effects may occur and these will generally increase the thermal conductivity. Thus, the plot of lattice conductivity against the superlattice period will show a minimum that is likely to occur at about 5 nm for the bismuth telluride system. It can be concluded that it will be unlikely to find a lattice conductivity below about 0.1 W/m K. It should be noted that the calculations by Lin et al. are specifically for quantum wires and the thermal conductivity is then probably limited by interface scattering rather than interface resistance. However, the lower limit for λ_L remains unchanged.

If we make use of the values for the electrical conductivity and the Seebeck coefficient that have been given by Lin et al., a power factor of $\alpha^2\sigma T$ is obtained which is equal to 41.9 W/m K at 77 K. Combining this result with a lattice conductivity of 2.9 W/m K yields the quoted value of six for ZT. If we change the value of λ_L to 0.1 W/m K, the figure-of-merit becomes substantially greater. To take full advantage of this smaller lattice conductivity, the carrier concentration must be reduced so that the Seebeck coefficient rises to a new optimum value of about $-630\ \mu$V/K, whereupon ZT becomes equal to about 20, as shown in Figure 10.1. There is some evidence from Heremans et al.[19] that such a high Seebeck coefficient can be obtained for Bi-based nanowires, although it is difficult to explain some of the very large thermoelectric voltages that have been observed by these authors.

We now consider the effect of changing the temperature. Lin[15] has suggested that there might be a smearing of the quantum effect at 300 K but we might suppose that the same model may still be used.

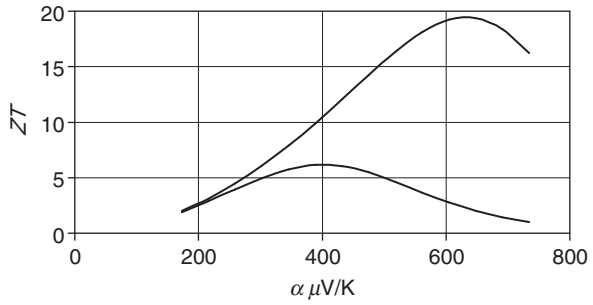

FIGURE 10.1 Plot of dimensionless figure-of-merit against Seebeck coefficient for Bi nanowires. Both curves are based data for the electronic properties provided by Lin.[15] The lower curve assumes a lattice conductivity of 2.9 W/m K while the upper curve assumes the minimum lattice conductivity of 0.1 W/m K.

If the necessary high Seebeck coefficient is to be reached, there must be a substantial energy gap. Lin et al.[14] have shown that the gap is greater than about 100 meV when the diameter of the wire is less than 10 nm and that it rapidly becomes larger as the wire becomes even narrower. Furthermore, there are Bi–Sb alloys that have a positive energy gap in the bulk state and they might be expected to have larger gaps than Bi as low-dimensional materials.

Of course, the mobility of the electrons falls as the temperature rises. It is expected that its value at 77 K will be 17.5 times its value at 300 K.[20] On the other hand, the density of states should be greater by a factor of 7.7 at the higher temperature and it should also be remembered that the temperature, T, appears directly in the dimensionless figure-of-merit. Taking these considerations into account, one calculates that ZT at 300 K should have 1.7 times its value at 77 K. Nevertheless, in view of Lin's remarks about the smearing of the bands, we shall be more conservative and suggest that, after optimization, Bi or Bi–Sb nanowires might have about the same values for ZT at both temperatures. We might go further and propose that ZT might have a limiting value of about 20 at all temperatures of practical interest.

It seems quite possible that the highest figure-of-merit will, in fact, be achieved using Bi or Bi–Sb nanowires. Bi is unusual in that the effective mass of the electrons in the trigonal direction is small but the average mass in the plane of the binary and bisectrix axes is quite large. Thus, there can be a high electron mobility along a nanowire combined with a reasonably large density-of-states resulting from confinement in a perpendicular direction. These advantages would be shared neither by a two-dimensional structure nor by a system of quantum dots. However, Lin and Dresselhaus[21] have calculated a high value for the figure-of-merit in superlattice nanowires, which are effectively linear arrangements of quantum dots. It seems likely that superlattice nanowires will have a lower value for the phonon conductivity than that in ordinary nanowires.

In Figure 10.2, the ratio of the coefficient of performance (COP) to that of a Carnot cycle is shown as a function of ZT. The lower curve corresponds to T_H/T_C equal to 1.5 while the upper curve is applicable when the temperature difference between the source and sink is very small. It should, in fact, always be possible to approach the upper curve by using a cascade, even when T_H/T_C is appreciably greater than unity. The COP would be as high as 35% of the ideal value for $ZT = 4$ and more than 60% of this value when $ZT = 20$.

10.5 Solid-State Thermionic Converters

Before we pass on to other matters we should discuss the prospects for using thermionic energy conversion in the solid-state. In other words, we must compare ballistic electron transport with diffusive transport. In fact, with some of the nanostructure configurations, it is expected that ballistic transport will be the predominating phenomenon.

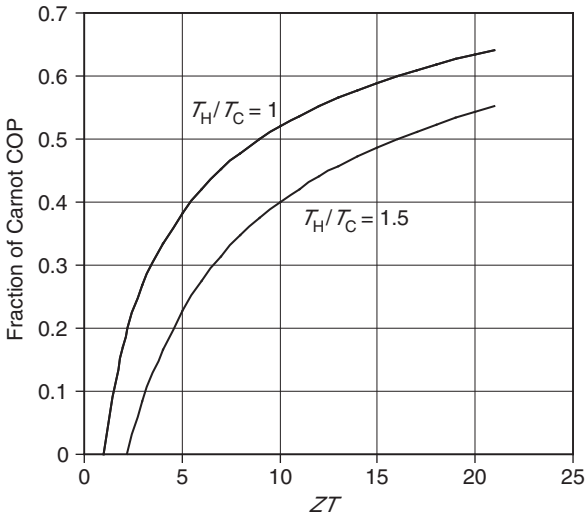

FIGURE 10.2 Plot of the COP of a thermoelectric refrigerator (as a fraction of the Carnot value) against *ZT*.

The thermoelectric and thermionic modes of operation have been compared by Ulrich et al.[22] for the two materials, InGaAs and Bi_2Te_3. In the thermoelectric mode of operation, the performance can be expressed in terms of a parameter β that depends on the carrier mobility, the density of states mass and the lattice conductivity.[23] Ulrich et al. showed that the same parameter can be used in the thermionic device. The optimum Fermi energy is closer to the degenerate region in the thermionic mode and this could be advantageous in narrow gap materials. However, in general, the value of *ZT* is higher for thermoelectric operation. It does not seem that the upper limit of the figure-of-merit can be improved by using a solid-state thermionic system. Previously, Vining and Mahan[24] had demonstrated that a thermionic device might be superior if a reduction in the lattice conductivity more than compensated for a deterioration in the electronic properties. Of course, this does nothing towards raising the upper limit of *ZT* above four since that value was obtained on the basis that λ_L is already as small as possible.

10.6 Possibility of Independent Electron and Phonon Currents

An alternative approach to the prediction of an upper limit for *ZT* has been adopted by Logvinov and Gurevich.[25] These authors have recognized that the conduction of heat by the phonons is a limiting factor for typical solid-state thermocouples. It is for this reason that there is considerable interest in vacuum diodes as energy conversion devices. However, Logvinov and Gurevich suggest that there can be a situation in which the phonon conduction in a semiconducting device can be eliminated. They point out that there is a characteristic thermal diffusion length (cooling length) below which the electron and phonon flows are independent of one another. For a sample that is shorter than this cooling length which is of the order of nanometers, the electron system may be regarded as being isothermal while the phonon system is adiabatic. In this case, the electron transport can be described by the usual theory but the phonon flow is absent. One then has one of the major advantages of a vacuum thermoelement without the problems of thermal emission and space charge.

The dimensionless figure-of-merit in the situation described by Logvinov and Gurevich is given by

$$ZT = \frac{\alpha^2 \sigma T}{\lambda_e} \tag{10.1}$$

Furthermore, $\lambda_e/\sigma T$ is given by the classical form of the Wiedemann–Franz law and is equal to $2(k/e)^2$, where the electron-free path length has been supposed to be energy independent. Then the

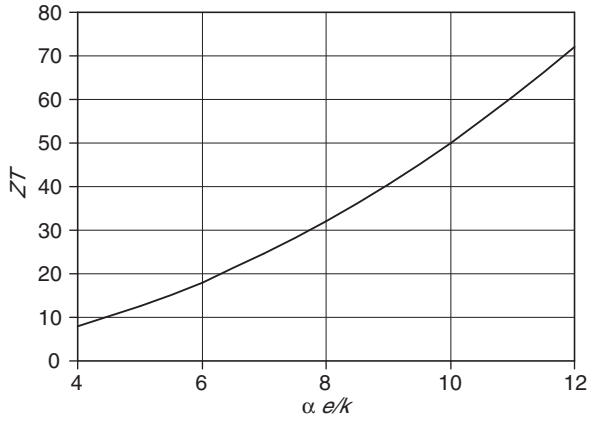

FIGURE 10.3 Plot of dimensionless figure-of-merit against dimensionless Seebeck coefficient in the absence of phonon conductivity.

Seebeck coefficient is given by

$$\alpha = \pm(2 - \eta)\frac{k}{e} \tag{10.2}$$

where η is the reduced Fermi energy. Then

$$ZT = (2 - \eta)^2/2 \tag{10.3}$$

This equation suggests that the figure-of-merit might increase without limit as $(-\eta)$ becomes larger, as shown in Figure 10.3.

There is, however, a certain limit that must be placed on the Seebeck coefficient. It has been shown[26] that the maximum value of this quantity lies close to $E_g/2eT$. If, for example, the energy gap is 1 eV, the highest Seebeck coefficient at room temperature is about 1.6 mV/K. This corresponds to a reduced Fermi energy of about -16. The limit on ZT that is placed by energy gap considerations is considerably larger than 100.

It is significant that the electrical conductivity would be extremely small for such a large value of the Seebeck coefficient. This might suggest that it would be difficult to pass sufficient electric current to produce a worthwhile Peltier effect. This effect would have to be large in comparison with radiation losses. Similar considerations set the minimum work function that can be tolerated in refrigerators based on the thermionic vacuum diode. It may not be necessary for the electrical conductivity to be very large if the length of the device is very small, as it is likely to be when the Logvinov–Gurevich condition is satisfied.

It remains to be demonstrated, of course, that lattice heat conduction can really be eliminated by reduction of the thermal path length. It is, perhaps, possible that the results of Ghoshal et al.[13] may be due in part to satisfaction of the Logvinov–Gurevich condition over part of the interface. Nevertheless, as Logvinov and his colleagues (unpublished data) have suggested, it will be extremely difficult to achieve the required adiabatic condition for the phonons. Somehow or other the phonon path between the heat source and sink has to be removed. Logvinov suggests the use of a thin dielectric layer through which electrons may penetrate by tunneling but, in fact, vacuum separation would seem to be needed. Thus, we think that it would be unwise to raise the ZT limit above 20 for the foreseeable future.

10.7 Vacuum Thermoelements

The reason for the high figures-of-merit that are predicted by Logvinov and Gurevich is the absence of heat conduction by the lattice. Such heat conduction is also absent in an energy converter based on the thermionic diode, or, as Ioffe described it, a vacuum thermoelement.[4]

Generation of electricity by vacuum diodes at high temperatures was demonstrated many years ago,[27] but heat transfer by radiation limits the performance in this region. However, Mahan[28] has shown that thermionic energy conversion above a temperature of 500 K would be possible using an emitter with a work function of 0.7 to 0.8 eV. For operation at room temperature, a work function of 0.3 eV would be needed. Such a small work function was, at one time, not thought to be possible but there is some evidence that it might exist in the compounds known as electrides and alkalides.[29] It would also be necessary for the distance between the anode and cathode to be rather less than 1 μm so as to avoid space charge problems. This means that there are substantial problems to be overcome before effective refrigeration and generation of electricity at ordinary temperatures can be achieved using thermionic diodes. Nevertheless, if these problems can be overcome, there is a great benefit from the avoidance of thermal conduction. At ordinary temperatures, the radiative transfer is not more than 10^3 W/m^2 while the thermionic cooling could be between 10^4 and 10^5 W/m^2. It has been shown[30] that the COP of a vacuum thermionic cooler with an emitter having a work function of 0.3 eV would be much better than that of a thermoelectric refrigerator with $ZT = 4$. In fact, the COP of a vacuum device with a work function of 0.3 eV would be very similar to that of a solid-state refrigerator having a ZT value of 20.[31]

Although it will be difficult to find an emitter with a work function of the order of 0.5 eV or less, there seem to be other possibilities for achieving the high thermionic currents that are essential for the operation of vacuum energy converters. For example, it has been suggested that tunneling from a semiconductor might be effective.[32–34]

The performance of a hypothetical thermionic refrigerator was calculated on the assumption that the return path for the electrons is provided by a metallic conductor. Xuan[35] has shown that some improvement might result from the use of a solid-state thermoelement for the return current. It is therefore possible that the energy converter of the future may combine the best of solid-state and vacuum technology.

10.8 Conclusions

It has been shown that there is no reason to raise the upper bound for the dimensionless figure-of-merit above four for bulk thermoelectric devices but there are good grounds for supposing that a value as high as 20 might be reached using low-dimensional structures. It is possible that a still greater value might be reached if one can realize the situation in which the electron and phonon flows are independent of one another. If, indeed, ZT were to reach a value of about 20, then the performance at ordinary temperatures would be similar to that of a vacuum diode with a cathode having a work function of 0.3 eV.

Acknowledgments

The author wishes to thank Yu-Ming Lin, Mildred Dresselhaus, Jeff Sharp, Yuri Gurevich, and George Logvinov for most helpful discussions. He has also received great encouragement from Hylan Lyon and George Nolas.

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